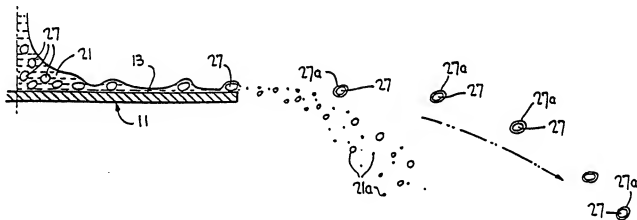




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁴ : B01J 13/02, A61J 3/07	A1	(11) International Publication Number: WO 85/ 0528 (43) International Publication Date: 5 December 1985 (05.12.85)
(21) International Application Number: PCT/US85/00827 (22) International Filing Date: 6 May 1985 (06.05.85) (31) Priority Application Number: 611,583 (32) Priority Date: 18 May 1984 (18.05.84) (33) Priority Country: US	(81) Designated States: AT (European patent), AU, BE (European patent), BR, CF (OAPI patent), CG (OAPI patent), CH (European patent), CM (OAPI patent), DE (European patent), DK, FI, FR (European patent), GA (OAPI patent), GB (European patent), HU, IT (European patent), JP, KR, LK, LU (European patent), ML (OAPI patent), MR (OAPI patent), NI (European patent), NO, SE (European patent), SI (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent).	
(71) Applicant: WASHINGTON UNIVERSITY TECHNOLOGY ASSOCIATES, INC. [US/US]; 8204 Brentwood Industrial Drive, St. Louis, MO 63144 (US). (72) Inventors: SPARKS, Robert, Edward : 1318 West Adams Avenue, Kirkwood, MO 63122 (US). MASON, Norbert, Simon; 645 Langton Drive, St. Louis, MO 63105 (US). (74) Agents: STERN, Marvin, R. et al.; Holman & Stern, Chartered, 2401 Fifteenth Street, N.W., Washington, DC 20009 (US).	Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	

(54) Title: METHOD AND APPARATUS FOR COATING PARTICLES OR LIQUID DROPLETS



(57) Abstract

Solid particles or viscous liquid droplets of core material (27) are encapsulated in a coating material (21) largely as single particles with a single coherent coating, by feeding a suspension of the two materials onto a rotating surface (13). The suspension is centrifugally dispersed by the rotating surface into relative large coated particles (27, 27a) and relatively small droplets (21a) of coating material. Only the size of the droplets of unused coating corresponds to the droplet formed from atomization of the liquid coating material. The size of the coated particles depends on the size of the uncoated particles and is much less dependent upon the atomization characteristics of the rotating surface. Upon being thrown from the rotating surface, or falling from that surface, the droplets (21a) and coated particles (27, 27a) are solidified by exposure to air and are separated by sieving, or the like. The solidified droplets of pure coating material may be recycled into the suspension. Coating of all particles is achieved by dispersing the individual components of core material in the coating material before the resulting suspension reaches the rotating surface.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GA	Gabon	MR	Mauritania
AU	Australia	GB	United Kingdom	MW	Malawi
BB	Barbados	HU	Hungary	NL	Netherlands
BE	Belgium	IT	Italy	NO	Norway
BG	Bulgaria	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali		
FR	France				

1 METHOD AND APPARATUS FOR COATING
2 PARTICLES OR LIQUID DROPLETS

3
4
5
6
7
8

9 BACKGROUND OF THE INVENTION

10 1. Technical Field

11 The present invention relates to a method and
12 apparatus for coating or microencapsulating solid
13 particles or viscous liquid droplets. More particularly,

1 the present invention relates to improvements in such
2 methods and apparatus which provide encapsulation
3 techniques and effects which are unprecedented in the
4 prior art.

5 2. Discussion of the Prior Art

6 Coating or microencapsulation of solid particles
7 or liquid droplets is widely employed to protect coated
8 substances from environmental effects and/or control
9 their release time and/or confer improved handling
10 characteristics. Typical products which are coated or
11 microencapsulated are drugs, pesticides, dyes, etc..

12 Numerous coating or microencapsulation techniques
13 have been employed in the prior art, many of which are
14 described in the Encyclopedia Of Chemical Technology,
15 third edition, volume 15, pages 470-493 (1981), John
16 Wiley and Sons. By and large, these techniques suffer
17 from one or more important disadvantages, including:
18 high cost; inapplicability for coating particles smaller
19 than 200 micrometers in diameter; complexity; long
20 contact time between the core and coating materials prior
21 to solidification of the coating material; inability to
22 achieve wetting and coating of the core particles with
23 the desired coating material; inefficient separation of
24 coated particles from unused coating material and

1 inefficient usage or wastage of coating material. Also
2 important in many methods are the tendency for the coated
3 particles to agglomerate and the limited choice of wall
4 materials. There are severe cost disadvantages to most
5 methods because they are batch processes difficult to
6 operate on large commercial scale and because they must
7 employ a solvent for the coating and are unable to use
8 melted coating materials, which require no solvent
9 removal or handling facilities.

10 There have been a number of attempts in the prior
11 art to provide coating techniques which are devoid of the
12 aforesaid disadvantages. For example, in U.S. patent
13 number 4,386,895 (Sodickson), there is disclosed a
14 rotating apparatus having radially-extending conduits
15 from which hollow needles project radially outward into a
16 reservoir of jelling material. As the apparatus spins,
17 liquid core material is urged by centrifugal force
18 through the conduits and needles. The liquid core
19 material is formed into droplets at the distal ends of
20 the needles, and the droplets are centrifugally thrown
21 into a layer of the gelling material which forms on the
22 outer reservoir wall due to the centrifugal forces
23 produced by rotation. The droplets of liquid core
24 material are thusly encapsulated by the gelling
25 material. This technique works well for its intended

1 purpose. However, it is limited to use with liquid as a
2 core material (i.e., it cannot be used to
3 microencapsulate solid particles) and the minimum size
4 droplet that can be coated depends upon the inner
5 diameter of the needle. As to the latter limitation,
6 there are practical limitations on minimum needle size,
7 particularly when viscous core liquids must flow
8 therethrough.

9 In U.S. patent number 2,955,956 (Baugh et al.), a
10 rotating disc or table is disposed below a feed pipe
11 through which a slurry composition of coating material is
12 fed. The slurry is spread over the spinning disc surface
13 to form a thin film of the coating material thereon. An
14 annular flow of solid granules is permitted to impinge
15 upon the film on the disc surface, whereupon the granules
16 are coated with the coating material. The coated
17 granules are thrown or are permitted to fall from the
18 rotating disc and are solidified by dry warm gas directed
19 at the falling granules. A second annular flow of
20 granules is directed onto the rotating film to scavenge
21 the unused film and assure that all of it is utilized.
22 Again, this technique is satisfactory for a limited
23 purpose, namely coating granules, such as salt, with
24 additives, but it cannot be readily employed to coat
25 liquid droplets. Moreover, since the granules in the

1 scavenging outermost annular flow cannot possibly be
2 coated to the same extent as granules in the innermost
3 flow, it is not possible with this technique to achieve
4 uniform coating of all of the granules. Therefore, the
5 Baugh et al. technique is more suitable for wide
6 dispersion of additives onto the surface of granules than
7 it is for coating particles.

8 British Patent No. 1,090,971 to Wilson, et al.,
9 discloses a method of microencapsulating solid particles
10 by forming a dilute suspension of the particles in a
11 dilute solution of a resinous coating material in a
12 volatile liquid, causing the suspension to impinge on a
13 spinning disc whereby the dilute suspension is dispersed
14 as a spray consisting of atomized coating solution and
15 microencapsulated particle droplets, the spray of
16 droplets then being exposed to steam at temperatures
17 above the boiling point of the coating solvent which
18 volatilizes the unwanted liquid solvent so as to leave
19 coated particles plus particles of pure coating of the
20 same size. The process, however, requires a feedstock
21 solution having a very low percentage content of
22 particles to be coated, involves the high temperature
23 removal of a large amount of unused feedstock liquid by
24 volatilization, and does not permit separation by sizing
25 of coated particles from particles of pure coating
26 material.

1 Objects and Summary of the Invention

2 It is therefore an object of the present invention
3 to provide an improved method and apparatus for coating
4 or microencapsulating both solid particles and viscous
5 liquid droplets.

6 It is another object of the invention to provide a
7 method and apparatus for microencapsulating particles
8 which enables at least a majority of the particles to be
9 coated individually or discretely rather than in clusters
10 while simultaneously providing improved means for
11 separating unwanted and unused liquid coating material
12 from the coated particles. More particularly, it is an
13 object of the invention to provide a coating process and
14 apparatus which includes controlled mechanical or
15 physical separation of coated particles from unused
16 liquid coating material by size discrimination, whereby
17 the method is equally applicable to the coating of solid
18 or viscous liquid particles, either with materials
19 including a liquid solvent or with molten coating
20 liquids, and whereby the wettability of the core
21 particles or droplets by the coating material is
22 relatively unimportant, permitting use of the method for
23 a wider variety of core particles and coating materials.

1 It is another object of the present invention to
2 provide a method and apparatus for coating or
3 microencapsulating solid particles and viscous liquid
4 droplets over a wide range of particle and droplet sizes,
5 including droplets and particles having diameters well
6 below 200 micrometers.

7 It is a further object of the present invention to
8 provide a method and apparatus for coating or
9 microencapsulating solid particles or viscous liquid
10 droplets with much less complexity, continuously, at a
11 much faster rate, and at lower cost than is possible in
12 much of the prior art, and to avoid the problem of
13 agglomeration of the particles being coated.

14 Still another object of the present invention is
15 to provide a method and apparatus for coating or
16 microencapsulating solid particles or viscous liquid
17 droplets wherein coating material can be easily re-cycled
18 back into the process if not used during a first pass
19 through the process.

20 It is yet another object of the present invention
21 to provide a method and apparatus for coating or
22 microencapsulating solid particles or viscous liquid

1 droplets in which coating thickness can be easily
2 adjusted by adjustment of any of plural process
3 parameters.

4 A further object of the present invention is to
5 provide a method and apparatus for coating or
6 microencapsulating solid particles or viscous liquid
7 droplets wherein the contact time between the core and
8 coating materials prior to solidification of the coating
9 material can be made sufficiently short to prevent
10 degradation of some labile materials, or to prevent their
11 dissolving one in the other when they are partially or
12 totally miscible.

13 The present invention provides, in a process for
14 coating particles with a liquid coating, a method for
15 obtaining individually coated particles while
16 simultaneously facilitating removal of the coated
17 particles from excess coating liquid with which the
18 particles are mixed in a suspension, the method
19 comprising feeding the suspension onto a rotating surface
20 to separate the suspension into coated particles and
21 atomized liquid droplets expelled circumferentially from
22 the surface, and rotating the surface at a speed yielding
23 a predominance of the droplets of undesired liquid
24 coating of a predetermined size which is smaller than the
25 size of the coated particles.

1 Thus in accordance with the present invention,
2 solid particles or liquid droplets of core material to be
3 coated are initially dispersed in molten or dissolved
4 coating material to form a suspension. The suspension of
5 the two materials is then fed to the surface of a
6 rotating disc, table or other rotating element. The
7 process parameters, particularly the speed of rotation of
8 the disc or other rotating element are controlled so that
9 the centrifugal forces imposed on the suspension by the
10 disc or the like cause the suspension to spread towards
11 the disc periphery with progressive thinning out of the
12 liquid and separation of excess coating material from the
13 coated particles, with dispersion of the suspension into
14 (1) large coated particles and (2) significantly
15 smaller-size atomized droplets of excess coating material
16 which are formed by atomization of the thin film of
17 liquid coating at the periphery of the disc or the like.
18 Thus, in accordance with the invention, the disc or the
19 like is used as a means for mechanically or physically
20 separating the excess coating liquid from the
21 individually coated particles and dispersing the
22 separated liquid as atomized droplets of significantly
23 smaller size than the coated particles. Most
24 importantly, to obtain the required separation and
25 dispersion, the invention involves relating the rotary
26 speed of the disc to the required size of atomized

1 droplets of excess liquid coating material to be obtained
2 from the disc, rather than relating the disc speed to the
3 size of coated particles to be obtained. This represents
4 a significant departure from known techniques involving
5 the use of a rotating wheel or the like to provide
6 dispersion of coated particles, where the wheel speed is
7 related to the required size of coated particle
8 products. In practical terms, for coated particles of
9 comparable dimensions, the invention involves rotary disc
10 speeds surprisingly in excess of those used in the prior
11 art techniques.

12 The average mean size required for the atomized
13 droplets of excess coating liquid may, in practice, be
14 determined by the amount of contamination, i.e., excess
15 unused coating material, which is acceptable in the final
16 product of coated particles, such determination being
17 effected by known techniques involving the relative sizes
18 of the coated particles and the particle size
19 distribution characteristics of unused coating liquid,
20 related to rotational speeds, liquid feed rate, length of
21 wetted periphery, and viscosity in rotary atomizer-type
22 equipment. Typically, in accordance with the invention,
23 the average size of atomized droplets may be about 20% to
24 75% of the size of the coated particles.

1 Since the materials being coated are solid (or
2 viscous liquid), they are not atomized but are simply
3 thrown from the disc as relatively large particles
4 retaining a coating of the liquid in which they were
5 immersed. The control of the process parameters to
6 provide separation of the suspension by the rotary disc
7 into individually coated particles and significantly
8 smaller droplets of excess coating material
9 differentiates the process of the present invention
10 completely from prior art processes such as spray
11 congealing, in which a slurry of dispersed solids is
12 atomized as a liquid, with the product solid present
13 inside the atomized droplets. In spray congealing the
14 dispersed solids are sufficiently finely divided that
15 there are many solid particles in most of the atomized
16 slurry product, and the size distribution of the entire
17 product approximates that predicted from atomization
18 correlations. In spray congealing, when the suspension
19 must behave as a liquid during atomization and no solvent
20 is subsequently removed, the volume fraction of solids in
21 the suspension (and hence, also in the product congealed
22 droplets) has an upper limit near 30%, while in the
23 present invention the volume fraction of coated solids in
24 the product particles may be in excess of 90%, owing to
25 the separation of the unused coating liquid on the
26 rotating disk and its atomization into smaller, easily

1 removed particles. In the present invention essentially
2 all of the solids in the feed slurry and all of the
3 coated product solids are larger than the sizes predicted
4 from atomization correlations for the processing
5 conditions employed. An example of the size distribution
6 of the feed solids, product solids and atomized coating
7 obtained is provided in Example VII.

8 The invention further has clear distinctions from
9 the old art of spray-chilling, in which a suspension is
10 atomized with subsequent solidification of the droplets
11 by cooling, and from spray-drying, in which a solvent is
12 present in the original suspension or solution and is
13 subsequently removed. In both these known processes, the
14 feed suspension or solution is atomized as a liquid, and
15 the products of the processes are the solidified
16 droplets, and there is no separation between particles
17 containing solids and those not containing solids. In
18 principle any atomization device can be used which will
19 give the desired droplets. In the present invention, the
20 process variables are adjusted to give a completely
21 different result, and products can be formed which are
22 impossible to form in general spray-chilling or
23 spray-drying. For example, it is convenient with the
24 process invention to place thin waxy coatings (e.g. 100
25 micrometers) around solid particles 2 millimeters in

1 diameter. In spray-chilling, it would not be possible to
2 pass the feed slurry through a pressure nozzle or
3 two-fluid nozzle, because the core particles would block
4 or plug the orifices in typical nozzles. If a very large
5 nozzle was used to permit the particles to pass, the
6 resultant coarse spray would include many product
7 particles containing no core (just large drops of
8 coating), a few core particles having thin coating, many
9 having thick coating and many in agglomerates rather than
10 as single coated particles. This would occur because
11 particle formation in these orifice devices occurs by
12 atomization of the entire slurry simply as a liquid which
13 happens to contain some solid particles. Such a slurry
14 of large particles could, of course, be passed over a
15 rotating-disc atomizer without any plugging or flow
16 stoppage. However, the disc would be run to treat the
17 slurry as a simple fluid, giving all atomized droplets in
18 the same size range. Again, this means that much of the
19 coating would be in the form of particles as large as the
20 coated particles and many of the particles will be in the
21 form of agglomerates. In none of these cases could most
22 of the unused coating be separated from the coated
23 particles by simple means such as sieving, and the
24 product would contain large inert particles of coating as
25 a major fraction. This is unacceptable in most practical
26 cases.

1 By contrast, in the present invention, with a feed
2 slurry containing e.g. 500 micron core particles, and a
3 desired coated product particle of 600 micron average
4 diameter, the disc size, rotational speed, feed rate of
5 the slurry and coating viscosity will be adjusted to
6 force all the unused coating to be in the form of
7 droplets much smaller (e.g. a mean diameter around 250
8 micrometers) so that most of it can be easily separated
9 from the product, and the product particles will
10 essentially be all in the form of single coated core
11 particles nearly all having an average coating thickness
12 of 50 microns. If it is desired, it is possible to make
13 the unused coating particles smaller, or somewhat larger,
14 while making the desired product.

15 A key point of the invention is to run the process
16 differently from a typical spray-chilling process. In
17 the latter process, the atomization is set to treat all
18 the feed slurry as a liquid, making droplets in the
19 desired size range. In the process invention, all
20 parameters are adjusted to force all unused particles
21 into a relatively small size, formed by atomization of
22 the film of pure coating, while the large product of
23 coated core particles is thrown off the disc surrounded
24 by the desired amount of remaining liquid, subsequently
25 solidified as a coating.

1 The small coating material droplets and the
2 coating-wetted particles resulting from operating the
3 disc in accordance with the invention are thrown or
4 caused to fall from the spinning surface and solidify due
5 to the drying or cooling effect of the surrounding air or
6 gas. Sieving or other size discrimination techniques
7 may be readily employed to remove the coated particles
8 from the much smaller particles of unused coating
9 material and the removal step is facilitated compared
10 with prior art processes because of the size
11 discrimination between the coated particles and the
12 smaller particles of excess coating material which is
13 conferred by the process invention. The coating material
14 particles thusly collected may be re-cycled into the
15 process. The minimum size of the solid particles or
16 liquid droplets which can be coated by this technique is
17 limited only by the size of the particles or droplets
18 themselves and by the lower limit of droplet size of
19 excess coating liquid which can be obtained with a
20 rotating disc (dry particles of 1-5 micrometers at high
21 disc speeds with low viscosity coatings containing
22 solvent). By completely dispersing the particles or
23 droplets in the molten coating material before the
24 materials are placed in contact with the rotating
25 surface, it is possible to coat all particles in a
26 similar fashion. The more uniform the size of the

1 dispersed particles the more particle-to-particle
2 uniformity there will be in the coated particles. This
3 has little effect on the size distribution of smaller,
4 atomized excess coating.

5 Brief Description of the Drawings

6 These and other objects, features and many of the
7 attendant advantages of the present invention will be
8 better understood upon a reading of the following
9 detailed description considered in connection with the
10 accompanying drawings wherein like parts in each of the
11 several figures are identified by the same reference
12 numerals, and wherein:

13 Fig. 1 is a diagrammatic illustration of apparatus
14 according to the present invention which may be employed
15 to perform the method of the present invention;

16 Fig. 2 is a diagrammatic illustration of an
17 alternative embodiment of the present invention;

18 Fig. 3 is a diagrammatic representation of still
19 another embodiment according to the present invention;

1 Fig. 4 is a diagrammatic representation of a
2 further embodiment employed in accordance with the
3 present invention;

4 Fig. 5 is a diagrammatic illustration of yet
5 another embodiment of the present invention;

6 Fig. 6 is a diagrammatic elevational view of a
7 rotary separating element showing its effect on a liquid
8 suspension when used in accordance with the invention;

9 Fig. 7 is a diagrammatic plan view of the element
10 shown in Fig. 6;

11 Fig. 8 is a view similar to Fig. 7 but showing
12 another type of rotary separating element;

13 Figs. 9, 10 and 11 are diagrammatic views of prior
14 art products (from a spray drying process) including
15 coated particles, the figures representing successive
16 stages in a coating process;

17 Fig. 12 is a view similar to Fig. 9 showing an
18 intermediate product according to the invention prior to
19 final separation of coated particles from droplets of
20 excess coating liquid; and

1 Figs. 13 to 15 are diagrammatic views of
2 alternative rotary separating devices useful in
3 performance of the invention.

4 Description of the Preferred Embodiments

5 Referring specifically to Fig. 1 of the
6 accompanying drawings, an enclosed spray chamber 10 (with
7 only top wall 12 illustrated in Fig. 1) is provided for
8 performing the method of the present invention. Within
9 chamber 10 there is disposed a rotatable disc or table 11
10 having an upper surface 13 which may be disposed
11 horizontally. Rotatable disc 11 is rotatably driven
12 about its central vertical axis by means of a variable
13 speed drive motor 17 acting through drive shaft 15. A
14 speed control unit 19 permits adjustment of the
15 rotational speed of the disc 11.

16 Speed control 19 and motor 17 may be located
17 inside or outside of chamber 10, depending upon the
18 particular application. The disc may be disposed above
19 the motor or suspended below the motor, with appropriate
20 modification of feed lines, supports, etc.

1 A reservoir 20 is adapted to contain molten or
2 dissolved coating material 21. The reservoir 20 is
3 heated, for example, by means of a heating coil 23
4 disposed about the reservoir periphery, to maintain the
5 coating material 21 in molten or dissolved form. In this
6 regard, the coating material 21 may be supplied to
7 reservoir 20 in molten form and maintained in that state
8 by means of the heating coil; alternatively, the coating
9 material may be supplied to the reservoir in solid form
10 and melted by the heat derived from heating coil 23. In
11 either case, the molten coating material 21 in the
12 reservoir is in a flowable state. A feed funnel 25 is
13 provided to extend through an opening in chamber 10 so as
14 to deliver individual mass components 27 of core material
15 (e.g., solid particles of core material) to be coated
16 into reservoir 20. In instances where the core material
17 is in the form of droplets of viscous liquid, funnel 25
18 may be replaced by a droplet-forming tube, a means of
19 feeding an emulsion or the like. A stirrer mechanism
20 extends into the chamber 10 and reservoir 20 and is
21 actuated by a variable speed stirrer motor 30 disposed
22 outside of chamber 20. The stirrer 22, when driven by
23 motor 30, acts to disperse the solid particles 27 (or
24 liquid droplets) of core material throughout the molten
25 coating material 21. The result is a slurry or
26 suspension of the two materials disposed in reservoir

1 20. This slurry or suspension is delivered through a
2 gravity-feed passage 31, extending from the bottom of
3 reservoir 20, to a ball valve mechanism 33. The ball
4 valve 33 is selectively actuatable from outside chamber
5 10 by means of actuating rod 35 to control the rate of
6 flow of the suspension material through the ball valve
7 33. It is noted that the heating coil 23 is disposed so
8 as to heat the suspension as it passes through passage
9 31 and ball valve 33, thereby assuring that the coating
10 material remains in its molten state while in these
11 components. The outlet passage 37 from ball valve 33 is
12 disposed directly above the axial center of surface 13 so
13 as to deliver the suspension material substantially along
14 the rotation axis of disc 11.

15 The space above surface 13 is heated, for example,
16 by means of industrial grade heat guns 39, to maintain
17 the temperature on surface 13 sufficiently high so that
18 the coating material in the suspension remains molten.
19 Additional heat is provided at the underside of disc 11,
20 for example, by means of infrared heat lamps 40. Heating
21 may be provided by many methods such as preheated air,
22 steam, radiant energy, induction heating, etc.

1 The top surface 13 of disc 11 may be smooth or may
2 be provided with a plurality of angularly-spaced
3 radially-extending grooves 24 defined therein, or raised
4 fins, so as to establish paths of travel for the material
5 deposited on surface 13 from ball valve 33. Grooved or
6 vaned surfaces are advantageous if the particles to be
7 coated are small, for example below 200 micrometers in
8 diameter, and the coating is viscous, because they can
9 produce finer particles of the unused liquid coating than
10 do smooth discs at the same rotational speed.

11 In operation, the coating material 21 in liquid or
12 slurry form is disposed in reservoir 20. If the coating
13 material 21 is a wax, the wax is melted by heating. If a
14 polymer coating material is used, it may be dissolved in
15 a solvent, if necessary. The coating liquid may contain
16 emulsified or suspended particles if they are desired in
17 the final wall or coating on the core particle. The core
18 material must be solid particles, granulated aggregates
19 of fine particles or droplets of liquid which is more
20 viscous than the liquid coating material 21. These
21 particles or droplets 27 preferably, but not necessarily,
22 should have a relatively narrow size distribution. When
23 the droplets or particles are fed into the slurry of
24 coating material 21, the stirrer 29 may be actuated by
25 stirrer motor 30 to disperse the particles 27 in the

1 material 21. With the particles properly dispersed (and
2 this may be a continuous process), the disc drive motor
3 17 is actuated and set to the desired speed by speed
4 control 19. This desired speed will depend primarily
5 upon the size of the smaller excess coating particles to
6 be produced as described below. Ball valve 33 is then
7 actuated by means of actuator rod 39 to permit the
8 suspension to flow onto the surface 13 of disc 11. Valve
9 33 is opened slowly until the desired flow rate is
10 achieved. The centrifugal force acting upon the
11 suspension material as it hits the surface 13 causes the
12 material to be thrown radially outward on the surface or
13 grooves 24. This has the effect of dispersing the
14 suspension into both particles 27 wetted with the coating
15 liquid and smaller droplets of coating liquid which do
16 not contain the core particles 27. The heating of the
17 region surrounding disc 11 maintains the coating material
18 in liquid state on surface 13. However, when the
19 material is thrown from or falls from disc 11, the
20 material falls through dry cooler air which causes the
21 coating material to solidify by cooling or drying. The
22 solidified small droplets of excess coating material and
23 the core material coated with the solidified coating
24 material fall to the bottom of the chamber during the

1 solidification process. Sieving, or other separation
2 techniques, may be employed to separate the coated
3 particles from the smaller particles of pure coating
4 material. The smaller coating material pieces may then
5 be recycled into the process by delivering such pieces
6 into reservoir 20. The majority of the original
7 suspended particles are coated discretely and similarly,
8 a feature which is achieved by virtue of the fact that
9 the original core material particles 27 are carefully
10 dispersed in the coating material before the suspension
11 is fed to the rotating disc. The coating thickness may
12 be varied mainly by changing the viscosity of the coating
13 liquid, but also by adjusting the feed rate of suspension
14 to the disc, by varying the rotational speed of the disc,
15 by varying the diameter of the disc or by varying the
16 number of grooves or vanes.

17 It is possible to perform the method of the
18 invention as a continuous process by feeding the coating
19 liquid 21 and particles 27 into reservoir 20 on a
20 continuous basis. An endless conveyor belt disposed at
21 the floor of chamber 10 collects the particles and feeds
22 them to a train of sieves which discriminate between
23 coated particles and the smaller particles of pure
24 coating material. The latter may be delivered directly
25 to the reservoir 20 whereas the coated particles may be

1 dispensed in any manner desired. Alternatively, all of
2 the particles may be pneumatically conveyed into a
3 cyclone, sieves or bag filter for separation of smaller
4 excess coating droplets to be recycled.

5 As previously noted, the process parameters are
6 specifically controlled, in a manner to be described, so
7 as to provide a separation of the liquid suspension by
8 means of the disc into coated particles (generally these
9 will be individually coated particles unless the process
10 is operated at low enough speed so that a small fraction
11 of the particles remain as doublets or triplets, or if
12 there is a wide size distribution of feed particles such
13 that the finer core particles are trapped in larger
14 particles) and droplets of excess coating liquid of
15 significantly smaller size than the coated particles.
16 The effect of the rotating disc on the suspension fed to
17 it is vividly illustrated in Figures 6 to 8. It will be
18 seen that the coating liquid 21 in the suspension is
19 gradually pulled away from the core particles 27, forming
20 a liquid film on the disc, as the suspension moves from
21 the center toward the periphery of the disc, with
22 progressive decrease in thickness of the liquid film or
23 sheet and finally separation of the excess liquid from
24 the particles 27, leaving a coating layer 27a on the
25 particles and dispersing the excess coating into a spray

1 of small droplets 21a formed from the thin coating film.
2 Figures 6 and 7 show this effect for a disc with a smooth
3 upper surface, and Figure 8 shows the effect with a
4 grooved disc. The size of the atomized droplets of
5 excess coating bears little relation to the size of the
6 solid coated particles, but depends rather on the film
7 spreading and atomization characteristics of the liquid
8 coating alone. The core particles, by contrast, move by
9 a totally different mechanism, not spreading into a film
10 but simply being thrown through or along the film of
11 coating, issuing from the disc periphery with a small
12 amount of associated coating material.

13 Figure 12 shows a typical product in accordance
14 with the invention as it is sprayed or expelled from a
15 rotating surface. It will be evident that the product
16 consists of core particles 27 with a liquid coating layer
17 27a all generally of similar size, and droplets 21a of
18 excess unused coating material 21 which are of
19 significantly smaller size than the coated particles and
20 which have a size distribution typical of that expected
21 for simple atomization of the pure coating liquid. The
22 product shown in Figure 12 is in vivid contrast to
23 typical products of prior art processes which use a
24 rotary wheel or the like to provide dispersion of

1 suspended particles. Thus, Figures 9 to 11 show the
2 product of a typical prior art process (spray drying) in
3 which particles are imbedded in droplets of a liquid
4 containing a solvent, by forming a slurry of the
5 particles in the liquid and forming droplets of the
6 slurry by feeding the slurry to a rotary wheel or the
7 like. As shown in Figure 9, the product as it leaves the
8 wheel contains particles 127 with a liquid coating 127a
9 and separated droplets 121 of excess coating material.
10 However, it will be evident that there is no sharp size
11 discrimination, as in products of the present invention,
12 between the coated particles (which are usually coated in
13 clusters, but some of which will be coated singly) and
14 the droplets of excess coating material. Thus, there are
15 a significant number of droplets 121 which are comparable
16 in size to the coated particles, in contrast to products
17 of the present invention where the droplets predominantly
18 are significantly smaller than the coated particles and
19 most large particles are coated discretely. Accordingly,
20 subsequent removal of excess droplets of coating
21 material, by sieving, centrifuging or the like, is
22 facilitated with products according to the invention
23 compared with the products of the prior art processes.
24 Figure 10 shows the prior art product of Figure 9 after
25 evaporation of the solvent, and Figure 11 shows the
26 product after removal of the smaller excess coating

1 droplets, for example by sieving, illustrating the rather
2 high percentage of unused coating material (in the larger
3 droplets thereof) which has not been removed from the
4 coated product. It is essentially impossible by this
5 prior art process to produce product particles with core
6 loadings above 50%, to remove excess coating, and to have
7 high particle-to-particle uniformity. Looked at in the
8 alternative, the invention provides a product comprising
9 relatively large, predominantly individually coated
10 particles and uncoated droplets predominantly of
11 significantly smaller size than the coated particles,
12 whereas prior art products are predominantly a mixture of
13 individual mass components of coated particles and
14 uncoated droplets of generally similar dimensions wherein
15 the core particles themselves are relatively small
16 compared to the final particles.

17 In order to obtain a product wherein there is a
18 sharp size discrimination between the coated particles
19 and the droplets of excess coating liquid, the process
20 parameters in accordance with the invention are
21 controlled in a particular manner. More particularly, in
22 accordance with the invention, the rotational speed of
23 the disc or the like is related to the average mean size
24 required for the droplets 21a (as will be described in
25 more detail below) rather than relating the rotational

1 speed of the disc or the like to the average size
2 required for the coated particles. By contrast, in the
3 prior art processes, the speed of the rotary wheel or the
4 like is related to the size required for the formed
5 droplets irrespective of whether they contain imbedded
6 core particles or not. Thus, in the present invention,
7 the disc or the like is run at surprisingly higher speeds
8 than in the prior art for producing coated core particles
9 of similar size to the particles of the prior art.

10 As noted above, in carrying out the invention, the
11 speed of rotation for the disc is related to the required
12 mean droplet size for the excess coating material rather
13 than to the required size of coated particles and in this
14 process, changes in the disc speed have significantly
15 less effect on the thickness of coating on the large core
16 particles. It is well known in industrial spray drying
17 and spray chilling techniques using rotary disc-type
18 atomizers that there are mathematical correlations
19 between the disc speed and the average droplet size
20 expelled from the disc, see for example pages 179-184 of
21 "Spray Drying Handbook" by K. Masters, 3rd Edition, John
22 Wiley & Sons, New York (1979), and which is specifically
23 incorporated herein by reference. These correlations may
24 be used to provide an estimate of required disc speed for
25 the present invention, (possibly incorporating a

1 viscosity correction factor in the correlations to
2 compensate for the effect of hot air flow as in Figures 3
3 and 4) once the desired average droplet size for the
4 excess coating liquid has been established. This desired
5 average droplet size may be established from known
6 droplet size distribution estimates, for example, using
7 log-probability graphs (also discussed in the above
8 reference) and relating the estimated droplet size
9 distribution to the acceptable contamination percentage
10 in the final product, i.e., the percentage of acceptable
11 excess coating droplets of a size making them impractical
12 to separate from the coated particles. Again, it should
13 be stressed that while techniques are known for
14 estimating disc speed in relation to a required droplet
15 size and for estimating droplet size distributions, these
16 have not previously been utilized in the present manner
17 whereby, in a particle coating process, disc speed is
18 related to a predetermined size required for the droplets
19 of excess coating liquid rather than being related to the
20 size required for the coated product particles
21 themselves. Also, it is understood that the correlations
22 referred to above for determining the required disc speed
23 may be used for estimation purposes, and in practice, it
24 may be desirable somewhat to adjust the disc speed
25 empirically.

1 To illustrate the significant difference in
2 rotational speeds used in processes according to the
3 invention compared with prior art processes, the various
4 parameters used in a typical prior art spray cooling-type
5 particle embedding process may be compared with the
6 parameters used in a process in accordance with the
7 invention for coating like particles with a like liquid
8 coating. Thus, for example, if it is required to coat
9 ion-exchange resin beads having a sieve fraction 53-106
10 microns with a wall material of 9/1 paraffin wax/Elvax
11 420 (Dupont ethylene-vinyl acetate copolymer, melt index
12 150) in a spray cooling procedure in accordance with a
13 typical prior art process, the rotational speed of an
14 8-inch diameter (0.2 meter) disc type atomizer typically
15 would be set at about 3,000 r.p.m. for a feed rate of 4.5
16 kg/hr of slurry containing 2/1 wt ratio of coating to
17 core particles, with a coating viscosity of 50 centipoise
18 to give an average fluid drop in the atomized slurry
19 close to the size just containing the largest core
20 particle. For the largest single core particle at 70%
21 loading in the final microcapsule, this droplet size
22 would be 120 microns and setting the rotational speed at
23 3,000 r.p.m. would give an average droplet size of about
24 118 microns from the correlation noted above. However,
25 this will be the average particle size in the atomized
26 slurry both for particles containing the core material

1 and also for droplets of the excess pure coating
2 material. A product obtained from this prior art process
3 at these conditions showed a substantial overlap in
4 particle size distribution of the coated particles and
5 the unused coating droplets so that it was not practical
6 to effect a separation based on size.

7 By contrast, in a process in accordance with the
8 present invention, if it is estimated that the smallest
9 microencapsulated product including the above beads will
10 have a diameter of 67 microns at approximately 50%
11 loading of the 53-micron core particle, the rotational
12 speed of a disc may be set for example to run at 8,000
13 r.p.m. to give an average particle diameter for unused
14 coating droplets of about 40 microns. To estimate the
15 amount of unused coating droplets which might be in the
16 microencapsulated product, a log-probability graph, as
17 described above may be used and results in a
18 contamination rate of about 10% for a product sieved at
19 67 microns. A run was also made under these conditions,
20 but using an 8-inch vaned disc giving somewhat smaller
21 droplets of excess coating. After sieving at 53 microns,
22 the contamination, measured by counting coated particles
23 and remaining pure coating particles, was approximately
24 7%.

1 The correlation referred to above with the
2 viscosity term modified to mirror the effect of hot air
3 moving over the surface is:

4

$$\bar{x} = \frac{(1.4 \times 10^4)(M_L)^{0.24}}{(Nd)^{0.83}(\pi d)^{0.12}} \left(\frac{V}{15} \right)^{0.1}$$

where \bar{x} = Average droplet diameter (microns)

M_L = Liquid feed rate (kg/hr)

N = Rotational speed (RPM)

d = Disk diameter (meters)

V = Viscosity (centipoise)

πd = Wetted periphery (meters). Use nh for disks with
n vanes or grooves h meters high.

5 As noted above, one of the parameters which may
6 be adjusted to vary the thickness of the coating material
7 on the final coated particle is the viscosity of the
8 coating liquid. In this regard, when wax is employed as
9 a coating material, the viscosity can be readily lowered

1 to thereby provide thinner coating walls on the final
2 coated particle, by adding solvents to the molten coating
3 material 21. When the inclusion of a polymeric material,
4 e.g., polyethylene in the coating is desirable the
5 viscosity can be lowered significantly through addition
6 of compatible materials of substantially lower viscosity,
7 e.g., waxes. In general, the solid particles 27 of core
8 material should be insoluble in the liquid coating
9 material 21; however, if the contact time between the
10 core material 27 and the coating material 21 is
11 sufficiently short before the coating material
12 solidifies, solids may be coated before they dissolve.
13 In this way, water soluble or water sensitive solids may
14 be coated by an aqueous solution. Likewise, droplets of
15 viscous liquids (i.e., of significantly greater viscosity
16 than the coating material 21) may also be coated.

17 In some applications the materials may be selected
18 such that the solid core material 27 reacts with the
19 coating liquid 21 so as to form an initial solid wall at
20 their juncture before the coating material 21 is
21 solidified during the process. Thus, the core material
22 27 might contain a polyfunctional acid chloride, or
23 isocyanate, and the liquid 21 might contain a polyamine
24 or polyol. This technique is also useful for coating a
25 liquid since the initial wall or shell formed by the

1 chemical reaction between the two materials prevents
2 absorption or dispersal of the core material into the
3 coating material or aggregation of the core particles
4 before the coating material solidifies.

5 Coatings of slurries may be formulated by
6 suspending the solids desired in the coating liquid prior
7 to, or simultaneously with, the suspension of the core
8 particles. Suspended solids in the coating may be
9 soluble in the coating if their contact time with the
10 coating is insufficient to permit dissolution.

11 Liquids may also be coated by dispersing them to
12 form a suspension or emulsion in the coating liquid. The
13 core liquid should have a viscosity higher than that of
14 the coating liquid so that the spread of liquid and
15 subsequent atomization into small drops occurs primarily
16 in the coating liquid. Liquid core materials may also be
17 coated after they are absorbed onto or into solids.

18 It is also possible to catch the coated particles
19 on a layer of powder or in a hardening or extraction bath
20 in which additional solvent is removed by extraction or
21 in which a chemical hardening reaction occurs. An
22 example of the latter would be the formation of

1 gelatin-coated particles which are caught in a bath
2 containing glutaraldehyde which hardens the wall or
3 coating material and greatly decreases the permeability
4 of the wall.

5 It is possible to use the invention to produce
6 walls of polymers which are insoluble in all or nearly
7 all solvents when the polymers are available in the form
8 of aqueous latex suspensions. Examples are acrylics,
9 rubber, synthetic rubber, polyvinylidene chloride, etc.
10 The solid or droplet core particles are suspended in the
11 latex and the suspension fed to the rotating element
12 according to the present invention. Moist air must be
13 blown over the disc surface or other means provided to
14 prevent the latex from drying and coagulating on the
15 disc. After the coated particles and smaller excess pure
16 latex particles leave the disc they are dried, e.g., by
17 falling through a chamber through which hot unsaturated
18 air or gas is passing. As water is removed from the
19 latex, the polymer particles coagulate into an insoluble
20 film. When dry the film coating is a tight barrier only
21 affected by solvents for the polymer.

22 Another embodiment of the present invention is
23 illustrated in Fig. 2 to which reference is now made. A
24 rotating disc 11 with a grooved top surface 13 and its

1 drive motor 17 are similar to like components illustrated
2 in the embodiment of the Fig. 1. Infrared heat lamps 40
3 are employed to heat the space above disc 11 and a
4 stirrer motor 30, having its speed controlled by a VARIAC
5 41, stirs the coating and core materials to provide the
6 necessary suspension. A heated funnel 45 is selectively
7 raised and lowered along three threaded vertical support
8 rods 49, only two of the support rods being illustrated
9 in Fig. 2. The stirrer 50 is disposed within funnel 45
10 and is rotated by means of drive shaft 47 connected to
11 stirrer motor 30. The distal end of shaft 47 is in the
12 form of a plug 51 which, depending upon the height of the
13 funnel 45 on support rods 49, may project through the
14 lower funnel opening and thereby close off outflow from
15 the funnel to the disc 11. This embodiment eliminates
16 the ball valve and provides flow control by means of the
17 raising and lowering of the funnel on shafts 49, or by
18 raising and lowering the motor. Many more feed schemes
19 will be apparent to those skilled in the art.

20 Another embodiment of the present invention is
21 illustrated in Fig. 3 to which detailed reference is now
22 made. A rotating disc 55 having a smooth flat upper
23 surface 57 is disposed horizontally between two
24 horizontal walls 59 and 60. A funnel 61 contains a
25 stirrer 63 placed to suspend solid particles in liquid

1 coating material which is added simultaneously to the
2 stirred funnel. The lower end of funnel 61 extends
3 through a suitably provided opening 65 in upper wall 59
4 so that the bottom opening of funnel 61 is disposed to
5 permit the funnel contents to fall on the disc surface 57
6 in alignment with the rotation axis of the disc. A
7 distribution cone 67 diverges downwardly and is disposed
8 substantially concentrically about the funnel stem so as
9 to prevent splashing of the slurry material delivered
10 from the funnel to the disc surface. Hot air is
11 channelled to the region between plates 59 and 60, both
12 above the disc 55 and below it, by means of suitable hot
13 air conduits 69 which communicate with suitable openings
14 in plates 59 and 60. The temperature of the air
15 delivered through conduits 69 is sufficient to maintain
16 the coating material in molten form when it is located in
17 the region between plates 59 and 60. It is apparent that
18 the plates aiding in controlling air flow need not be
19 parallel. For example, higher hot air velocity at the
20 edge of the rotating disc can be achieved with the gap
21 between plate and rotating disc decreasing as the radius
22 increases. It is also apparent that the plates may
23 rotate in common with the disc.

24 In the Embodiment of Fig. 3, the funnel 61 serves
25 as the vessel in which the solid particles or liquid
26 droplets of core material are dispersed in the coating

1 liquid. In addition, the feed rate of the resulting
2 suspension from the funnel onto disc surface 57 is
3 controlled by the level of suspension maintained in the
4 funnel rather than by a funnel outlet valve mechanism.

5 The embodiment of Fig. 4 is similar in many
6 respects to the embodiment of Fig. 3 except for the
7 suspension feeding mechanism and for the fact that the
8 disc is tilted at an angle, e.g., forty-five degrees,
9 relative to horizontal. The suspension of coating and
10 core materials is disposed in a vessel 70 having a
11 stirrer 71 therein. A lower corner portion of the vessel
12 70 is selectively openable to permit controlled feeding
13 of the suspension material onto the top surface 57 of
14 disc 55. Fig. 4 is intended to illustrate that the disc
15 can be oriented at substantially any desired angle and
16 need not be horizontal as shown in Figs. 1 - 3.

17 The embodiment of Fig. 5 diagrammatically
18 illustrates the use of a generally conical mesh screen 77
19 disposed above the top surface of a disc 75 so as to
20 converge to a location between the disc and the lower end
21 of a funnel 73. The funnel delivers the suspension
22 material toward the disc 75 in the manner described above
23 in relation to the embodiments of Figs. 1 - 3. However,
24 the mesh screen 77, which rotates with disc 75, is

1 provided to aid in controlling the average coating
2 thickness by draining away part of the coating material
3 through the screen. Further forms of rotary discs 90,
4 92, 94 which may be used for the invention are shown in
5 Figs. 13 to 15. In addition, multi-tier rotating discs,
6 vaned wheels, grooved discs and radial tubes can be
7 employed.

8 The invention as described hereinabove is suitable
9 for coating particles of substantially any shape;
10 however, the most uniform coating is obtained with
11 spherical particles. Particle size may generally vary in
12 the range from 10 micrometers to 10 millimeters, although
13 special designs or conditions will permit the use of
14 particles outside this range. Nearly spherical
15 particles may be readily formed by techniques well known
16 in the prior art, such as spray drying or prilling, by
17 extrusion or compression in molds, or by agglomeration of
18 fine powders in rotating drums using a liquid phase
19 binder and/or heat. It is also known that compact
20 crystals approaching a spherical shape may be obtained by
21 attrition during crystalization.

22 The preferred coating material for minimum process
23 cost should be liquid at coating temperature and should
24 solidify when cooled, without requiring either

1 evaporation of a solvent or a chemical reaction. The
2 viscosity of the coating material may range from 0.5 to
3 100,000 centipoises, with preferred viscosities between
4 1-5,000 centipoises. Preferred coating liquids are
5 various mixtures of polyolefins, ethylene-vinyl acetate
6 copolymer and waxes. A typical coating liquid
7 composition is 50 percent by weight polyethylene of
8 density 0.92, melt index 250, and 50 percent paraffin wax
9 having a melting point of 60° C. It is preferable that
10 the core material is insoluble in the coating liquid at
11 coating temperature, although soluble cores can be coated
12 if the contact time with the coating before spraying and
13 solidification is sufficiently short to prevent
14 dissolution.

15 During a typical operation, as noted above, the
16 particles to be coated may constitute up to 45 percent by
17 volume of the overall suspension slurry, although in
18 general the percent by volume will be in the 20-35%
19 range. The temperature surrounding the top surface of
20 the disc must be above the melting point of the coating
21 material. Typically, this may be between 60° and 90° C
22 for pure waxes and 120° to 160° C for polymer/wax
23 mixtures.

1 The rotational speed of the disc is chosen so that
2 the excess coating material produces much smaller spheres
3 than the coated particles. If the disc were used simply
4 as an atomizer for the coating liquid it is these small
5 spheres which would be produced. Since the excess liquid
6 wall material forms smaller droplets, the aerodynamic
7 drag force per unit mass is much higher than that for the
8 larger coated particles. Hence, as these smaller
9 droplets solidify they are slowed down much more quickly
10 by the drag force as they move away from the spinning
11 disc. These droplets, therefore, fall much closer to the
12 spinning disc. A receiver may be placed near the disc to
13 catch these small unused coating particles for recycling
14 back to the coating reservoir. Alternatively, the unused
15 coating particles may be caught in the inner portion of
16 the bottom cone for sieving and recycling.

17 When the ring of unused coating particles partly
18 overlaps the ring of coated particles, the particles
19 cannot be totally separated by sieving. When this
20 occurs, an increase in rotational speed of the disc
21 causes a separation of the rings, by throwing the coated
22 particles farther and decreasing the size of the unused
23 coating particles so that they fall closer to the disc.
24 When the product particles are less than 100 microns in
25 diameter, both the product and the smaller excess coating

1 particles fall within a few feet of the disc and are both
2 strongly affected by the air blowing outward along the
3 radius of the disc. Hence they do not separate cleanly
4 into distinct rings. However, they are easily separated
5 by sieving, centrifugal force, etc.

6 For particles in the range of 0.5 millimeter
7 diameter and a density of 1.2, a rotational speed of
8 1,000 - 1,500 rpm for a disc of 8 inches diameter
9 provides good spatial separation of the fine excess wax
10 particles from the much larger coated particles so that
11 the excess wax particles may be collected separately and
12 may not require a separate sieving operation.

13 The particles to be coated may be mixed with the
14 melted coating material immediately before the resulting
15 suspension is fed to the disc. Feeding rates for a disc
16 having an 8 inch diameter are preferably on the order of
17 100 milliliters to 5 liters per minute but can cover the
18 range of 10ml/min to 100 liters/min. For coating
19 materials with melting points substantially above room
20 temperature (e.g., above 50° C), the coated particles
21 solidify rapidly after leaving the disc surface and may
22 be collected immediately. If a solution is used as the
23 coating, then the solvent has to be evaporated before
24 essentially dry particles can be collected.

1 The embodiments described above include a disc
2 having a grooved surface, a disc having a flat smooth
3 surface, cupped or cone-shaped surface, and angled
4 screens or perforated plates disposed above a reservoir
5 (rotating or non-rotating). It is also possible to
6 provide a vaned disc whereby the disc comprises a
7 plurality of angularly spaced vanes with gaps
8 therebetween. Virtually any rotating device which can be
9 used for atomization may be used in the present
10 application, as long as the slurry does not have to pass
11 through a fine orifice where plugging may occur.

12 Other alternatives are an inverted cone made from
13 stainless steel screen and a vaned disc in which the
14 vanes are placed at an angle to the disc diameter.

15 In employing the invention, we have successfully
16 coated the following substances: phosphors (12-60
17 micrometers), potassium chloride angular particles
18 (25-300 micrometers), potassium chloride (approximately
19 spherical particles 500-860, 250-500, 120-250
20 micrometers), water thickened with carboxymethyl
21 cellulose, sucrose crystals (1-1.5 millimeters), sucrose
22 spheres (1.4-2 millimeters), aspirin powder (held
23 together with carboxymethyl cellulose solution),

1 acetaminophen (180-320 micrometer spheres), etc..
2 Coating liquids which we have employed include pure wax,
3 wax with solvents (e.g., paraffin wax 20 percent, Polywax
4 500 30 percent, 1,1,2, trichloroethane 50 percent), wax
5 mixtures (Polywax 500 16 percent, ethylene vinylacetate
6 copolymer (Elvax 420, 18% vinyl acetate, Du Pont de
7 Nemours, Inc.) 24 percent and paraffin wax 60 percent;
8 or paraffin wax 17 percent, Polywax 500 33 percent and
9 Elvax 420 50 percent), polyethylene wax, wax and low
10 density polyethylene (paraffin 50 percent and
11 polyethylene 50 percent), Woods metal (50 percent
12 Bismuth, 25 percent Lead, 12.5 percent Cadmium and 12.5
13 percent Tin), cellulosic polymer dissolved in a solvent,
14 and solutions of mixtures of waxes, polyethylene and
15 ethylene-vinyl acetate copolymer in aromatic and
16 aliphatic hydrocarbons. Coating materials have also been
17 used in the form of slurries containing up to 37 mass
18 percent of suspended insoluble solids, both smaller than
19 and greater than the average final wall thickness.

20 The present invention is further illustrated by
21 the following examples:

EXAMPLE I

In this example, nearly spherical particles of potassium chloride were used, the particles being of a 20-32 mesh (500-863 micrometers) fraction obtained by sieving. The apparatus was substantially that illustrated in Fig. 1 with the top surface of disc 11 smooth rather than grooved. The outlet opening 37 for the ball valve was disposed approximately $1/8$ inch above the surface 13 of the disc. The entire reservoir was heated by electrical tape and was equipped with a thermocouple. The disc was inclined at about 45 degrees from horizontal (as in the Fig. 4 embodiment) to increase the path of the upward-directed particles in the air so as to allow them to solidify before encountering a solid surface. (The downward-directed particles were not collected). The disc assembly was equipped with three heat guns above the disc and two below the disc in addition to the two heat lamps.

Thirty-eight grams of paraffin wax (Fisher P-22), 38 grams of Polywax-500 (made by the Bareco Division of Petrolite Inc.), and 24 grams of Elvax 420 (DuPont) were melted and mixed in a beaker. The molten wax and 38 grams of potassium chloride particles were mixed in the heated mixing reservoir. With all the heat guns on, the

1 disc was then turned on to rotate at 700 rpm. The valve
2 was opened to allow the suspension to flow onto the
3 center of the disc from which it was dispersed. Coated
4 potassium chloride was thrown in an upward trajectory
5 (because of the angle of the disc with respect to
6 horizontal) landing at floor level roughly six feet away
7 from the disc. The smaller pure wax particles followed a
8 path much closer to the disc, separated by one or two
9 feet from the coated potassium chloride particles.

10 The large particles were separated into three
11 fractions by sieving. Twenty-eight percent were greater
12 than 860 micrometers in diameter; 68% were between 590
13 and 860 micrometers in diameter; and 4% were less than
14 590 micrometers in diameter. The small wax particles
15 immediately around the disc were not recovered.

16 The mean diameter measured for a small number of
17 uncoated particles ($n=15$) was 521 ± 44 micrometers. The
18 coated particles had a mean diameter of 759 plus or minus
19 74 micrometers ($N = 15$). Therefore, the mean wall
20 thickness based on these measurements was 119
21 micrometers.

22 In the fraction having a diameter greater than 860
23 micrometers, all the particles sank in a liquid of
24 density approximately 10% greater than that of the wax

1 (i.e., diethyl succinate having a density of 1.047 grams
2 per cubic centimeter). This indicates that all these
3 particles contained potassium chloride. In the particles
4 having diameters in the range of 590-860 micrometers,
5 three particles out of twenty randomly chosen particles
6 floated, indicating that they were pure wax. (The
7 fraction of pure wax particles in this size range could
8 be decreased by higher disc speed or lower coating
9 viscosity). Water extraction showed that the fraction
10 having diameters greater than 860 micrometers contained
11 54.7% potassium chloride, and 45.3% wax; the fraction
12 having 590-860 micrometer diameter contained 65%
13 potassium chloride and 35% wax.

14 Whereas the free potassium chloride dissolved
15 within seconds when placed in water, less than 3% of the
16 coated potassium chloride (of either size fraction)
17 dissolved in ten minutes. Only 16.2% dissolved in 70
18 minutes from the 590-860 micrometer fraction, and 30.9%
19 dissolved in 70 minutes from the fraction having
20 diameters greater than 860 micrometers. In 266 minutes,
21 39% dissolved from the fraction in the range of 590-860
22 micrometer diameter, and 62% from the fraction having
23 diameters in the range greater than 860 micrometers.
24 This indicates that the soluble potassium chloride
25 particles were well coated.

1 In this example (I) the potassium chloride was
2 well coated by the waxy polymer coating. This is
3 difficult by methods such as fluid-bed coating because
4 the waxy droplets do not wet the potassium chloride
5 surface well. Hence, the coating spreads poorly over the
6 surface. In the present invention, the particles start
7 by being totally immersed in the coating, and the process
8 is so rapid that the coating does not have sufficient
9 time to uncover the surface before solidifying.

10 EXAMPLE II

11 Non-pareil sugar spheres ranging from 1.2 to 2
12 millimeters in diameter were encapsulated in wax having
13 the following composition: Gulfwax (household paraffin
14 wax) 38 grams; Polywax 500 (Bareco) 38 grams; and Elvax
15 420 (DuPont) 24 grams. While the wax was stirred at 104°
16 C in the mixing vessel, 40 grams of non-pareil spheres
17 were added, mixed well and the dispersion was poured on
18 to the disc, which was spinning at 1140 rpm. The
19 resulting wax coating on the coated non-pareils ranged
20 from 17 to 25% by weight when measured by extraction.
21 Uncoated non-pareil spheres released 73.6% of their
22 contents in ten minutes and 91% in thirty minutes.

1 Coated spheres did not release a detectable amount in ten
2 minutes (i.e., less than 1%). After thirty minutes, 1.1%
3 was released, and after one hour 2.6% was released.
4 Hence, the sugar was well coated.

5 EXAMPLE III

6 Twenty grams of cellulose acetate butyrate
7 (Eastman CAB 381-2) were dissolved in a mixture of 100
8 milliliters dichloromethane and 10 milliliters acetone
9 and placed in reservoir 20. Red sugar crystals having a
10 total weight of 28 grams and passing through a 500-micron
11 sieve but retained by a 250-micron sieve were mixed with
12 the CAB solution and the suspension fed to the disc
13 rotating at 1170 rpm without heating. The red particles
14 were well separated from the smaller, uncolored polymer
15 droplets during the coating operation. The fraction of
16 the coated product passing a 1 millimeter sieve but
17 retained by 860 micrometer openings (coated particles
18 agglomerated on the receiving surface due to inability to
19 evaporate all the solvent in the laboratory air) were 68%
20 sugar and 32% cellulose acetate butyrate coating. When
21 placed in water, 33% of the sugar dissolved in ten
22 minutes, and 65% in 90 minutes.

EXAMPLE IV

In order to coat with polymeric compositions of higher melt viscosity (e.g., polyethylene), it is necessary to control the air temperature adjacent to the rotating disc. This was achieved to a greater extent using the embodiments of Figs. 3 and 4 wherein the cover plates 59 and 60 were employed. Hot air (for example, from heat guns) is conducted directly through conduits 69 toward the disc.

100 grams of polyethylene (melt index = 250) was melted in a beaker. 34 grams of spherical granules of slightly water-soluble organic acid, having a number mean diameter of 0.740 millimeters, was mixed with the molten polyethylene. The temperature of the mixture was 154° C. This was delivered to the disc which was rotating at 1140 rpm. The temperature of the plates facing the disc ranged from 130° to 170° C at different points. The viscous suspension was fed to the plate over a period of five minutes. 46 grams of material which did not contact a wall were recovered and were distributed as follows:

	<u>Diameter (Micrometers)</u>	<u>% of total</u>	<u>Content</u>
1			
2	500	7.8	Polyethylene only
3	500-590	0.9	Polyethylene only
4	590-860	7.3	coated organic acid
5	860-1000	14.5	coated organic acid
6	1000-1180	9.1	coated organic acid
7	1180 particulate	3.7	several spheres
8	non particulate	56.7	"taffy" and "spider
9			webs", polyethylene
10			containing no organic
11			acid.

12 (The non-particulate material is not observed at lower
13 coating viscosity, but higher temperature could not be
14 employed in this example to lower the viscosity owing to
15 the thermal instability of the core particles).

16 For comparison, the particle size distribution of the
17 uncoated organic acid spheres was as follows:

1 The distribution of particle sizes was as follows:

2	<u>Diameter (micrometers)</u>	<u>Wt/(gm)</u>	<u>Content</u>
3	Below 500	26.3	metal dust
4	500-590	21.8	spheres
5	500-860	10.0	spheres and flat
6			pieces
7	Above 860	37.1	agglomerates

8 The spheres were covered with the metal as
9 determined by visual observation, but the potassium
10 chloride dissolved readily, indicating that the coating
11 was porous. Under the microscope the coating was seen to
12 consist of many small metal crystals, giving the
13 likelihood of leakage at crystal boundaries.

14 EXAMPLE VI

15 50 gm Polyethylene USI (density = 0.927, melt index
16 = 250) was dissolved in 50 gm Gulfwax Paraffin at 150°C.
17 The flat, smooth 8-inch diameter disc was held at 130°C

1 and rotated at 1,800 rpm. 50 gm of nearly spherical
2 acetaminophen particles, 177 - 250 micrometers was mixed
3 with the polymer/wax solution. The 177 - 300 micrometers
4 product fraction contained mostly coated single
5 particles.

6 EXAMPLE VII

7 The cone-screen embodiment of Fig. 5 was employed
8 in coating nearly spherical KCl. The percent core
9 material relative to total particle (i.e., payload)
10 increased in the product from a run made under the same
11 conditions using a flat disc. This demonstrates that the
12 porous cone represents another means to control wall
13 thickness by increasing the amount of coating liquid
14 drained away from the core particles, and also decreases
15 the fraction of excess coating liquid atomized from the
16 edge of the rotating device. There is, however, a
17 decrease in the number of discretely coated particles.

18 Coating composition was 38% by weight paraffin wax
19 (Gulf), 38% by weight Polywax 500, Bareco, and 24% Elvax
20 420 (Dupont). Original particle size range was 0.50 to

1 86 mm. The slurry was fed to the disc or rotor at 116
 2 degrees centigrade, with the air between the plates kept
 3 at 129-133'C.

4	<u>% Payload</u>	
5	<u>500-590 micrometers</u>	<u>590-850 micrometers</u>
6	Flat Disk	75.8
7	Cone Screen	57.3
		82.8

8 For the smooth disc, operated at the same
 9 conditions the size distributions of uncoated core
 10 particles, coated particles and atomized excess coating
 11 were as follows:

12	Uncoated KCL		
13	<u>Diameter (micrometers)</u>	<u>Weight (gm)</u>	<u>%</u>
14	Smaller than 420	.418	2.5
15	420-500	2.354	14.0
16	500-590	13.187	78.6
17	590-860	0.654	3.9
18	Larger than 860	<u>0.172</u>	<u>1.0</u>
19	Total	16.785	100.0

1 Product (in two rings around rotating device):

2 Coated KCL Particles (Outer Ring)

3	<u>Diameter (micrometers)</u>	<u>Weight (gm)</u>	<u>%</u>
4	Smaller than 500	.3	1.8
5	500-590	.6	3.6
6	590-860	12.1	73.4
7	860-1.00	2.6	15.8
8	1.00-1.18	0.5	3.0
9	Greater than 1.18	<u>0.4</u>	<u>2.4</u>
10	Total	16.5	100.00

11 Atomized Excess Coating (Inner Ring)

12	<u>Diameter (micrometers)</u>	<u>Weight (gm)</u>	<u>%</u>
13	Smaller than 149	1.0	5.5
14	149-177	0.9	5.0
15	177-250	1.5	8.3
16	250-297	3.3	18.3
17	297-420	7.3	40.6
18	420-500	1.3	7.2
19	Greater than 500	<u>2.7</u>	<u>15.1</u>
20		18.0	100.00

1 There is only a small overlap in the size
2 distribution of the large coated KCL particles (mostly
3 single coated particles) and the small droplets, which
4 consist mostly of atomized pure coating material. Since
5 solid KCL is more dense, nearly all coated KCL particles
6 would be in the outer circle. If the disc is operated at
7 higher rotational speed or if the viscosity of the
8 coating is decreased, the diameter of the atomized
9 droplets in the inner ring decreases. The diameter of
10 the ring containing the large coated particles will
11 increase if rotational speed is increased, or will
12 decrease slightly if speed is kept the same but viscosity
13 is decreased, because they have a thinner coating.

14 We have described an improved method and apparatus
15 for coating or microencapsulating solid particles or
16 viscous liquid droplets applicable to a wide range of
17 sizes. The coating technique works well for coating
18 solids in the 20-300 micrometer range where prior art
19 methods of spraying the coating onto fluidized particles
20 work poorly or not at all. In general the method is less
21 expensive than prior art processes because it is very
22 rapid and requires less energy and process control.
23 Contact time between the coating material and the core
24 material can be maintained extremely short. In addition,
25 the particles need only be handled once in the apparatus
26 as opposed to many passages through the spray region of
27 the spray coating methods.

1 The present invention is also useful in place of a
2 variety of other processes for forming microcapsules.
3 For example, the method of the present invention obviates
4 the need for careful control and timed changes in
5 conditions required in many cases of coacervation and
6 solvent evaporation microencapsulation processes. The
7 present method avoids the difficulties of microcapsule
8 agglomeration, a frequent problem in these processes.

9 The method of the present invention is also useful
10 with dispersed liquid core droplets, made more viscous
11 than the coating liquid to limit the spreading and
12 atomization phenomena to the less viscous coating
13 material. In this manner, the process of the present
14 invention may be employed to form microcapsules similar
15 to those formed by the annular-jet method.

16 Having described several embodiments of the new
17 and improved method and apparatus for coating or
18 microencapsulating solid particles or viscous liquid
19 droplets in accordance with the present invention, it is
20 believed that other modifications, variations and changes
21 will be suggested to those skilled in the art in view of

1 the foregoing description. It is therefore to be
2 understood that all such variations, modifications and
3 changes are believed to fall within the scope of the
4 invention as defined in the appended claims.

1 WHAT IS CLAIMED IS:

2 Claim 1. A method of coating or encapsulating
3 individual mass components of core material having the
4 form of solid particles, aggregates formed by granulation
5 or liquid droplets with a coating of material that is
6 less viscous than the core material and solid at normal
7 room temperatures but liquid at elevated coating
8 temperatures, or in the form of a solution during the
9 coating process, said method comprising the steps of:

10 distributing said individual mass components of
11 core material throughout the liquid coating material to
12 form a suspension;

13 feeding the suspension onto a rotating surface
14 which centrifugally separates and disperses the
15 suspension into (1) droplets of pure coating material and
16 (2) individual components of said core material coated
17 with said coating material;

18 cooling the coated individual mass components or
19 removing solvent therefrom to solidify the coating
20 material;

21 and controlling the process so as to produce a
22 predominance of the droplets of excess liquid coating as
23 droplets of a predetermined size smaller than the size of
24 the coated individual mass components.

1 Claim 2. The method according to Claim 1 wherein
2 the step of controlling the process includes relating the
3 speed of rotation of the surface to said predetermined
4 size of the droplets.

5 Claim 3. The method according to Claim 1 further
6 comprising the step of separating said coated individual
7 mass components from the droplets of pure coating
8 material.

9 Claim 4. The method according to Claim 3 wherein
10 the step of separating includes sieving or use of
11 centrifugal force to separate the relatively large coated
12 individual mass components from the relatively small
13 droplets of coating material.

14 Claim 5. The method according to claim 3 wherein
15 the step of separating includes rotating said rotating
16 surface at sufficiently high speed such that the droplets
17 of pure coating material are significantly smaller than
18 the coated individual mass components and therefore fall
19 from said rotating surface at a location radially inward
20 from the separated coated individual mass components.

1 Claim 6. The method according to Claim 1 wherein
2 the step of cooling or removing solvent includes passing
3 the coated mass components through ambient air or gas,
4 heated or unheated, by centrifugally hurling the
5 components from said rotating surface.

6 Claim 7. The method according to Claim 1 further
7 comprising the step of heating the region at said
8 rotating surface to maintain the coating material in
9 liquid form at said rotating surface.

10 Claim 8. The method according to Claim 7 wherein
11 the step of heating includes passing hot air between a
12 plate or plates positioned a short distance above and
13 below said rotating surface, or heating said plate or
14 plates by induction.

15 Claim 9. The method according to Claim 1 wherein
16 the step of distributing comprises the steps of:

17 heating said coated material in a vessel to
18 sufficiently high temperature to maintain the coating
19 material in liquid form;

20 dispersing said individual mass components of core
21 material into said coating material in said vessel; and

22 stirring the contents of said vessel to form said
23 suspension of individual mass components distributed
24 throughout said coating material.

1 Claim 10. The method according to Claim 1 wherein
2 the rotating surface is oriented at an acute angle
3 relative to horizontal.

4 Claim 11. The method according to Claim 1 further
5 comprising the step of adjusting the thickness of the
6 coating material on said core material by adjusting the
7 rotational speed of said surface.

8 Claim 12. The method according to Claim 1 further
9 comprising the step of adjusting the thickness of the
10 coating material on said core material by adjusting the
11 viscosity of the liquid coating.

12 Claim 13. The method according to Claim 1 further
13 comprising the step of adjusting the thickness of the
14 coating material on said core material by adjusting the
15 rate at which said suspension is fed onto said rotating
16 surface in said step of feeding.

17 Claim 14. The method according to Claim 1 further
18 comprising the step of adjusting the thickness of the
19 coating material on said core material by adjusting the
20 wetted surface of the rotating device.

1 Claim 15. The method according to Claim 1 further
2 comprising the steps of:

3 draining a portion of said coating material, which
4 is fed as part of said suspension to said rotating
5 surface, by providing porosity in said rotating surface
6 as with a mesh cover or porous material or perforated
7 material disposed in the form of a cone or bowl in spaced
8 relation above a further receiving surface;

9 centrifugally dispersing the coated mass
10 components, which are larger than the interstices or
11 perforations of said mesh cover, along said mesh cover
12 while partially draining the liquid coating material, by
13 gravity, such on and/or centrifugal force, away from the
14 coated mass components as the mass components move along
15 the mesh cover; and

16 passing said liquid coating through the mesh cover
17 and recycling the passed liquid coating material.

18 Claim 16. The method according to Claim 1 further
19 comprising the steps of:

20 solidifying said droplets of coating liquid by
21 centrifugally projecting them from said rotating surface
22 through ambient air or gas (heated or unheated, depending
23 on whether the coating is a melt or a solution);

24 collecting the solidified droplets of coating
25 material; and

26 recycling the collected droplets of coating
27 material.

1 Claim 17. The method according to Claim 1 further
2 comprising the steps of:

3 solidifying said droplets of coating material; and
4 recycling the solidified droplets of coating
5 material by returning them to said suspension.

6 Claim 18. The method according to Claim 1 further
7 comprising the step of adding a solvent for said coating
8 material to dissolve the coating material prior to or
9 during the formation of the suspension to permit coating
10 or to reduce the thickness of the coating material on
11 said coated mass components.

12 Claim 19. The method according to Claim 1 wherein
13 said core material is insoluble in said coating material.

14 Claim 20. The method according to Claim 1 wherein
15 said core material is at least partially soluble in said
16 coating material, and wherein the time from initial
17 contact between said core and coating materials to
18 solidifying of said coating material is sufficiently
19 short to prevent significant dissolution of said core
20 material into said coating material.

1 Claim 21. The method according to Claim 1 wherein
2 the core material or a component contained thereon reacts
3 with the coating material or a component contained
4 therein to form an initial solid wall at the periphery of
5 each individual mass component before said coating
6 material solidifies.

7 Claim 22. The method according to Claim 1 wherein
8 said core material is in the form of liquid droplets
9 having a higher viscosity than that of the coating
10 material.

11 Claim 23. The method according to Claim 1 further
12 comprising the step of hardening the coated mass
13 components by transferring them to a chemical hardening
14 bath.

15 Claim 24. The method according to Claim 23
16 wherein said coating material is a gelatin and said
17 hardening bath includes glutaraldehyde.

18 Claim 25. The method according to claim 23
19 wherein the coating is gelatin and hot gas, air or
20 non-solvent liquid is contacted with the gelatin to cause
21 cross-linking and insolubilization.

1 Claim 26. The method according to Claim 22
2 wherein said individual mass components are generally
3 spherical particles having diameters in the range of 10
4 micrometers to 10 millimeters.

5 Claim 27. The method of claim 1 wherein the
6 coating liquid is a suspension containing fine insoluble
7 particles which become part of the coating on the core
8 particles, and are equally as well distributed in the
9 excess coating liquid.

10 Claim 28. The method according to Claim 1 wherein
11 said suspension is flung radially outward along said disc
12 surface in radially-extending angularly-spaced grooves
13 formed in said surface.

14 Claim 29. In a process for coating particles with
15 a liquid coating, a method for obtaining individually
16 coated particles while simultaneously facilitating
17 removal of the coated particles from excess coating
18 liquid with which the particles are mixed in a
19 suspension, the method comprising feeding the suspension
20 to a rotating surface to separate the suspension into
21 coated particles and atomized liquid droplets expelled
22 circumferentially from the surface, and rotating the

1 surface at a speed for obtaining a predominance of the
2 excess pure coating droplets of a predetermined size
3 which is smaller than the size of the coated particles.

4 Claim 30. The invention of Claim 29 wherein the
5 volume percentage of particles to be coated in the
6 suspension is in the range 10-35%, preferably 20-35%.

7 Claim 31. The invention of claim 29 wherein
8 coated particles of temperature-labile material
9 (chemicals, enzymes, biological cells) are formed with
10 simultaneous formation of smaller droplets of excess
11 coating material, so rapidly that little or no
12 degradation or denaturation occurs.

13 Claim 32. The invention of claim 29 wherein the
14 core mass components to be coated are poorly wetted by
15 the coating liquid (wetting angle less than 90°) but are
16 completely coated by virtue of having been completely
17 immersed while in suspension and having the process of
18 liquid spreading and particle radial passage and
19 solidification occur too rapidly for the uncovering of
20 the core to occur.

1 Claim 33. A product comprising (a) individual
2 mass components of core material having the form of solid
3 particles, aggregates formed by granulation, or liquid
4 droplets coated or encapsulated in a liquid core
5 material, and (b) droplets of pure liquid coating
6 material of significantly smaller size than the coated
7 mass components, the product being produced by the
8 process as claimed in claim 1.

9 Claim 34. Apparatus for coating or encapsulating
10 individual mass components of core material having the
11 form of solid particles, aggregates formed by
12 granulation, or liquid droplets with a coating of
13 material that is less viscous than the core material and
14 solid at normal room temperatures but liquid at elevated
15 coating temperatures, or in the form of a solution during
16 the coating process, said apparatus comprising container
17 means for containing the individual mass components of
18 core material and the liquid coating material in the form
19 of a suspension, feed means for feeding the suspension
20 from the container means onto a rotating surface for
21 centrifugally separating and dispersing the suspension
22 into (1) droplets of pure coating material and (2)
23 individual components of said core material coated with
24 said coating material, cooling means for cooling the
25 coated individual mass components or for removing solvent

1 therefrom to solidify the coating material, and means for
2 controlling the apparatus to produce a predominance of
3 the droplets of excess liquid coating as droplets of a
4 predetermined size smaller than the size of the coated
5 individual mass components.

6 Claim 35. The invention of claim 34 wherein the
7 controlling means includes means for relating the speed
8 of rotation of the surface to the predetermined size of
9 the droplets.

10 Claim 36. The invention of claim 34 including
11 means for separating the coated individual mass
12 components from the droplets of pure coating material.

13 Claim 37. The invention of claim 34 including
14 heating means for heating a region at said rotating
15 surface for maintaining the coating material in liquid
16 form at the rotating surface.

FIG. 1

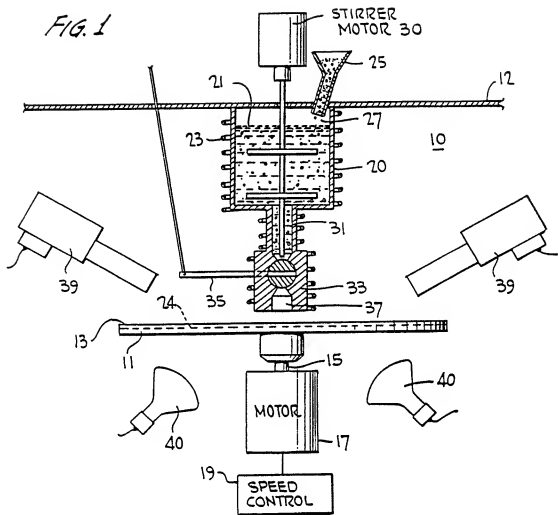


FIG. 2

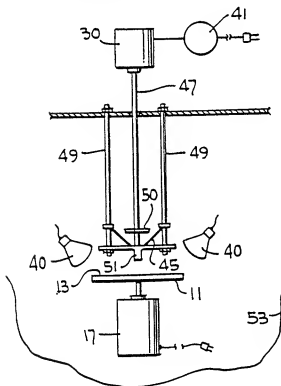
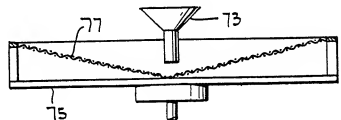


FIG. 5



2 / 4

FIG. 3

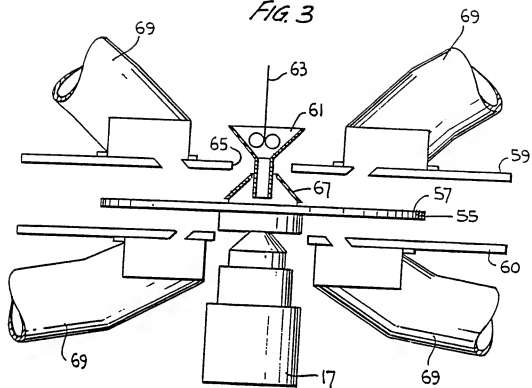
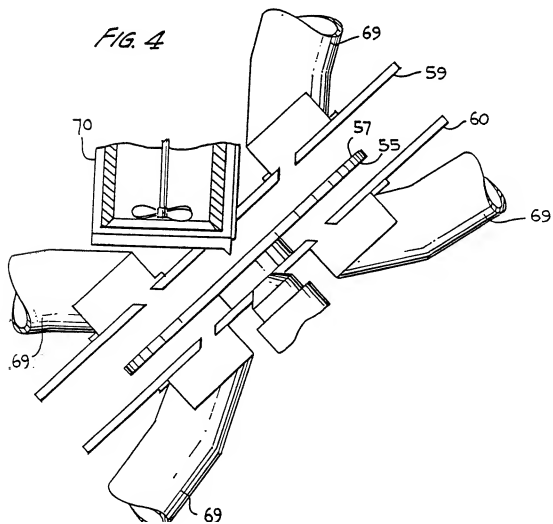


FIG. 4



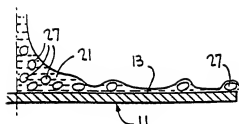


FIG. 6

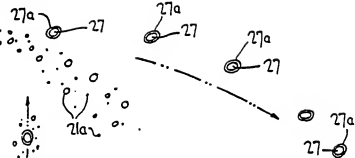


FIG. 7

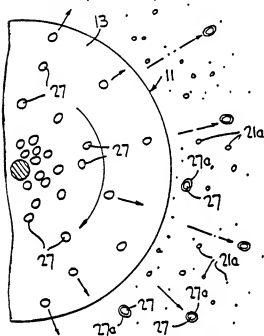


FIG. 8

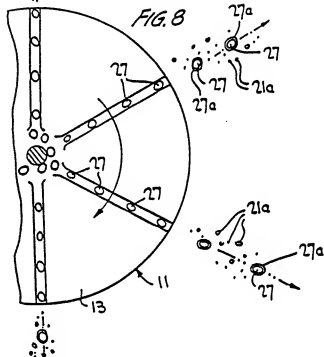


FIG. 9 (PRIOR ART)



FIG. 10 (PRIOR ART)

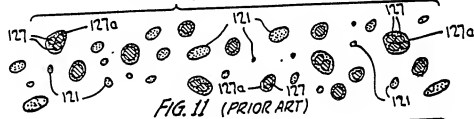


FIG. 11 (PRIOR ART)



FIG. 12

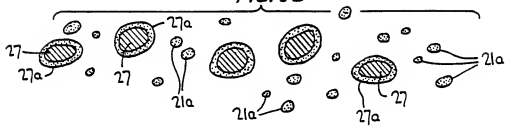


FIG. 13

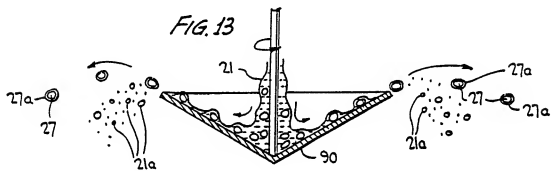


FIG. 14

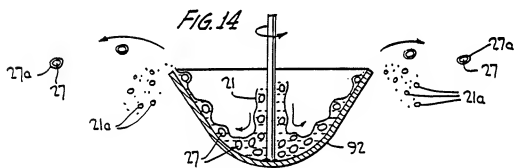
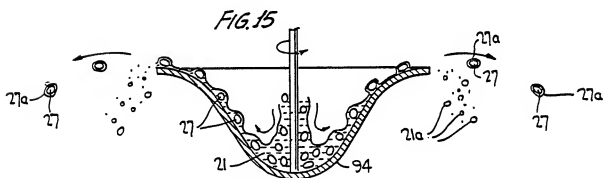


FIG. 15



INTERNATIONAL SEARCH REPORT

International Application No PCT/US 85/00827

I. CLASSIFICATION OF SUBJECT MATTER (It several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁴ : B 01 J 13/02; A 61 J 3/07		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	B 01 J A 61 J	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category *	Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 4123206 (CLARENCE C. DANNELLY) 31 October 1978, see column 3, lines 14-68; column 4, lines 1-43; figure 1 --	1,2,3,4,5,6,10,11,16,17,29,33,34,36
A	US, A, 4386895 (LESTER A. SODICKSON) 7 January 1983, see column 3, lines 33-68 (cited in the application) --	1,2,19,23,26,28,29,34,35
A	US, A, 2955956 (CHARLES BAUGH et al.) 11 October 1960, see column 3, lines 39-69 (cited in the application) --	1,6,8,16,19,34
A	GB, A, 873757 (VITAMINS LTD) 26 July 1961, see page 2, lines 68-130; page 3, lines 1-20 --	1,2,6,24
A	Derwent, volume 75, nr. 1, 4 February 1975, Section C: "Agricultural Chemistry", Derwent Publication Ltd. (London, GB) & JP, B, 49049294 (CHISSO CORP.) 26 December 1974, see abstract --	1,15
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
26th August 1985	27 SEP 1985	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	 G.L.M. Kuylenberg	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	DE, B, 1185109 (VITAMINS LTD.) 7 January 1985, see column 7, lines 10-65; figure 2 ---	1,7,9,34
A	FR, A, 1433421 (DUNLOP RUBBER CO.) 21 February 1966 & GB, A, 1090971 see page 1, left-hand column, paragraph 2; page 6, left-hand column, paragraph 3 (cited in the application) -----	1

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 17/09/85

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publicatio date
US-A- 4123206	31/10/78	US-A- 4218409	19/08/80
US-A- 4386895	07/06/83	None	
US-A- 2955956		None	
GB-A- 873757		None	
DE-B- 1185109		None	
FR-A- 1433421		GB-A- 1090971	